Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Rate Constants in the Free-Radical Polymerization of Perdeuterated Styrene

Gilbert Clouet[a]; Pierre Chaffanjon[a]
[a] Institut Charles Sadron (CRM-EAHP), Strasbourg-Cedex, France

To cite this Article Clouet, Gilbert and Chaffanjon, Pierre(1990) 'Rate Constants in the Free-Radical Polymerization of Perdeuterated Styrene', Journal of Macromolecular Science, Part A, 27: 2, 193 — 212

To link to this Article: DOI: 10.1080/00222339009351496

URL: http://dx.doi.org/10.1080/00222339009351496

J. MACROMOL. SCI.—CHEM., A27(2), pp. 193-212 (1990)

RATE CONSTANTS IN THE FREE-RADICAL POLYMERIZATION OF PERDEUTERATED STYRENE

GILBERT CLOUET* and PIERRE CHAFFANJON

Institut Charles Sadron (CRM-EAHP)
6 rue Boussingault
67083 Strasbourg-Cedex, France

ABSTRACT

Kinetic studies of the AIBN- and BPO-initiated free-radical polymerization of perdeuterated styrene (S-D8, styrene[α,β,2,3,4,5,6-$^2H_8$]) at 30–90°C were carried out. The average lifetimes of growing PS-D8 radicals in the photosensitized polymerization of the monomer were determined at 15, 20, and 25°C by the rotating-sector technique. The propagation rate constant k_p was found to be $3.63 \times 10^7 e^{-31500/8.314T}$ and the termination rate constant k_t to be $2.55 \times 10^{10} e^{-14200/8.314T}$. The activation energy for the propagation reaction of S-D8 is fairly close to that of styrene (S-H8), but the activation energy for the termination step of S-D8 is 1.5 times higher than that for S-H8. The deuterium isotopic effect on the rates of the polymerization was found to be inverse at all temperatures studied.

INTRODUCTION

The influence of the isotopic effect of deuterium substitution on the rate of free-radical polymerization has been reported for some deuterated monomers [1-4]. In most cases the rate of propagation, R_p, was found to be higher for the deuterated monomer than for the H-monomer. This is also the case for the following substituted styrenes, [α-^{2}H], [β-$^2H_2$], and

[2,3,4,5,6-$^2H_5$] [3], for which the magnitude of the isotope effect at 60°C depends on the position of the deuteriums. An exception has been reported for the styrene [4-^{2}H] where no such effect was observed [2]. The effect is usually ascribed to a secondary deuterium inverse isotope effect on the propagation step, neglecting the effect on the termination step.

On the other hand, some studies on the radical polymerization of D5-deuterated methyl methacrylate have shown that the isotopic substitution has a great influence on the mode of termination [5, 6]. The latter results prove that the isotopic effect on the termination reaction is more important than was previously thought.

In this work, we examine the rate constants k_p and k_t for the free-radical polymerization of styrene-D8 and discuss the influence of substitution on the propagation and termination reaction rates.

EXPERIMENTAL

Materials

Styrene-D8 received from Norsk-Hydro and styrene-H8 received from Norsolor (CDF chimie) were purified by double vacuum distillation over CaH_2.

Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

Benzoyl peroxide (BPO) was recrystallized from a chloroform-methanol (50-50) mixture.

Determination of Densities

The densities of styrene-D8 at 20, 25, 35, and 40°C ± 0.01°C were measured with a digital densitometer DMA 02.

Densities of polystyrene-D8-styrene-D8 solutions (0 to 5 wt% in polymer) at 25 and 35°C were measured with the same densitometer as above.

The polystyrene-D8 used in the previous solutions had molecular weights: $\overline{M}_n$ 460 000 and $\overline{M}_w$ 1 550 000. The polymer was prepared by bulk polymerization with a mixture of benzoyl peroxide and dicumyl peroxide at 80-140°C and high conversion, which explain its broad $\overline{M}_w$ distribution.

Polymerization

All the polymerizations were done in bulk.

Steady-State Condition

Rates of polymerization were followed gravimetrically. Polymerizations were carried out in sealed evacuated tubes, 10 mm o.d. × 150 mm, to which the required quantities of BPO or AIBN and 2 mL styrene (D8 or H8) were added. The contents were degassed by three freeze-thaw cycles and sealed off at a pressure of 0.1 torr. Polymerizations were effected in an electrically controlled 5-L oil bath at six temperatures, ±0.1°C, between 30 and 90°C (Pt thermometer). The temperature in the tube was measured for a test polymerization, and no difference with the oil temperature was noticed after the heating period. After the desired time of polymerization (chosen long enough to make the influence of the heating and cooling periods negligible), the tubes were removed and chilled in liquid nitrogen. Then the remaining monomer was distilled off under vacuum (10^{-6} torr). The polymers were dried at 50°C under vacuum (10^{-6} torr) for a minimum of 12 h.

The conversions were lower than 10% for all the polymerizations.

Nonsteady-State Conditions

The average lifetimes of growing radicals were determined by the rotating-sector method while the rate of polymerization was followed by dilatometry.

After purification, the styrene-D8 was degassed by three freeze-thaw cycles and introduced under argon into a double-walled cell, 35 mm i.d. × 45 mm, with two Pyrex windows and equipped with a calibrated capillary. The initiator was AIBN, and the solution was magnetically agitated.

The UV light was provided by mercury-xenon lamp, the bandwidth of which was confined to the 340 and 400 nm region by using a combination of various filters.

The sectors were made of an aluminum disk, 160 mm in diameter, divided into four sectors, with every second sector cut out to a radial depth in such a way that the ratio of the length of the light period to the length of dark period was 1/3. The disk was driven by a motor, by means of which the disk speeds could be varied from 1 to 4500 rpm. Lower speeds (less than 1 rpm) were obtained by a stepdown gear set.

The theoretical curves were calculated from the Matheson equations [7] by a computer.

RESULTS AND DISCUSSION

The customary simplified derivation of the kinetic equation for the radical polymerization of vinyl monomers is based upon three steps: initiation, propagation, and termination. The assumed equality of the absolute values of the rates of initiation and termination yields, in principle, the steady-state concentration of free radicals which, when substituted in the propagation rate equation, yields the overall rate equation for the polymerization.

Initiation by radical initiators:

$$\mathrm{I} \xrightarrow{fk_d} 2\mathrm{R}^{\bullet}, \tag{1}$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_1} \mathrm{RM}^{\bullet}, \tag{2}$$

$$R_\mathrm{I} = 2fk_d[\mathrm{I}]. \tag{3}$$

Propagation:

$$\mathrm{RM}_n^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{R{-}(M)}_n\mathrm{{-}M}^{\bullet} \equiv \mathrm{M}_{n+1}^{\bullet}, \tag{4}$$

$$-d\mathrm{M}/dt = R_p = k_p[\mathrm{M}]\,[\mathrm{M}^{\bullet}]. \tag{5}$$

Termination:

$$\mathrm{M}_i^{\bullet} + \mathrm{M}_j^{\bullet} \xrightarrow{k_t^d} \mathrm{M}_i + \mathrm{M}_j \tag{6}$$

or

$$\mathrm{M}_i^{\bullet} + \mathrm{M}_j^{\bullet} \xrightarrow{k_t^c} \mathrm{M}_i\mathrm{M}_j, \tag{7}$$

$$R_t = k_t[\mathrm{M}^{\bullet}]^2, \text{ with } k_t = k_t^d + k_t^c \tag{8}$$

Here $[\mathrm{M}^\bullet]$ denotes the concentration of the free radical species: f is the fraction of initiator decomposed that leads to chain initiation; k_d, k_p, and k_t, are the rate constants for the first-order decomposition of the peroxide, for the propagation, and for the termination, respectively; $[I]$ is the concentration of the initiator; and [M] is the concentration of the monomer.

In addition to this elementary scheme, a series of secondary steps could modify the kinetics as follows.

Chain termination by primary radicals:

$$\mathrm{R}^\bullet + \mathrm{M}_n^\bullet \rightarrow \mathrm{R{-}M}_{n}. \tag{9}$$

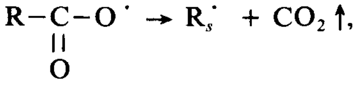
Induced decomposition of the initiator:

$$\mathrm{I} + \mathrm{M}_n^\bullet \rightarrow \mathrm{R{-}M}_n + \mathrm{R}^\bullet. \tag{10}$$

Transfer to the initiator:

$$\mathrm{I} + \mathrm{M}_n^\bullet \rightarrow \mathrm{M}_n + \mathrm{I}^\bullet. \tag{11}$$

Secondary decomposition of peroxide and initiation by secondary radicals (R_s):



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O}^\bullet \rightarrow \mathrm{R}_s^\bullet + \mathrm{CO_2}\uparrow, \tag{12}$$

$$\mathrm{R}_s^\bullet + \mathrm{M} \rightarrow \mathrm{R}_s{-}\mathrm{M}^\bullet. \tag{13}$$

The use of small quantities of initiator minimizes the induced decomposition and the transfer of initiator (Eqs. 10 and 11).

At 60°C and higher, initiation of styrene-H8 by secondary radicals can be neglected for benzoyl peroxide [8]. By analogy, this should also be the case for styrene-D8.

The thermal initiation of monomers was neglected at all temperatures, based on measurements of the thermal initiation rate of polymerization for styrene D8 and on values of Goldfinger [9] for styrene-H8. The maximum error on the overall initial rate at the lowest initiator concentrations was found to be less than 1.5%.

The combination of Eqs. (3), (5), and (8) yields

$$-d\mathrm{M}/dt = R_p = k_p/k_t^{1/2}(2fk_d)^{1/2}[\mathrm{M}]\,[\mathrm{I}]^{1/2}. \tag{14}$$

Steady-State Kinetics

The kinetics of polymerization of styrene-D8 in bulk in the presence of AIBN between 30 and 50°C, and of benzoyl peroxide (BPO) between 70 and 90°C, were studied. In order to take in account the changes of monomer and initiator concentrations, Eq. (14) has been integrated to give the following relation:

$$\ln([M_0]/[M]) = \beta(1 - e^{-(k_d t/2)}), \tag{15}$$

where

$$\beta = 2(k_p/k_t^{1/2})(2f[I_0]/k_d)^{1/2}. \tag{16}$$

Plots of Eq. (15) (Fig. 1) gave straight lines, from which β could be calculated (Table 1). Plots of ln β vs ln I_0 between 30 and 90°C give straight

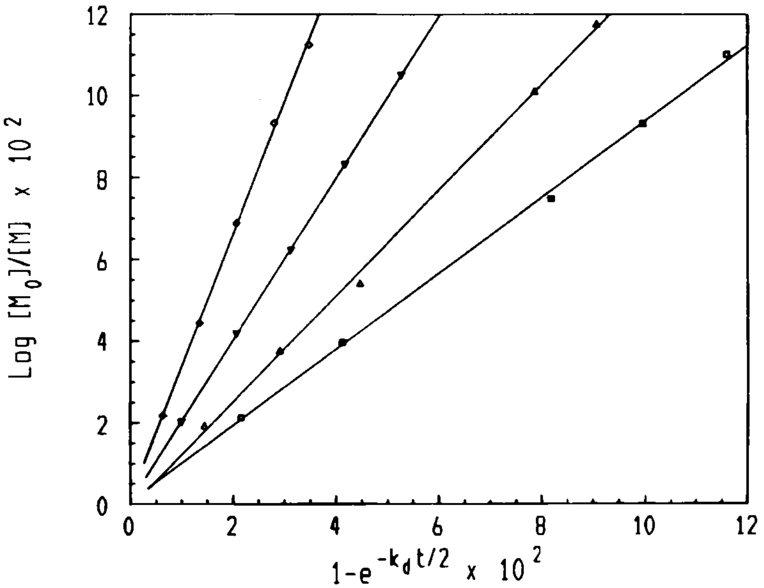


FIG. 1. Plot of ln ($[M_0]/[M]$) as a function of ($1 - e^{-(k_d t/2)}$) for the polymerization of styrene-D8 at four AIBN concentrations (in mmol/L): (□) 0.49, (△) 0.97, (▽) 2.4, (◇) 6.8, at 48.4 ± 0.1°C.

TABLE 1. Rates of Polymerization of Styrene (S-H8) and of Perdeuterated Styrene (S-D8)

Monomer	Temperature, °C	$[I] \times 10^3$, mol/L	β^a	$\bar{P}_n$
S-D8	28.4	0.495	2.449	—
		0.990	3.307	—
		2.475	5.258	—
		6.931	8.880	—
	48.4	0.485	0.929	9110
		0.971	1.296	6610
		2.426	1.980	5120
		6.794	3.230	3160
	68.4	0.672	1.251	3200
		0.951	1.431	3030
		2.301	2.333	2140
		6.709	3.932	1490
	78.4	0.665	0.782	2850
		0.960	1.015	2080
		1.897	1.340	1730
		3.847	1.958	1250
	83.4	0.643	0.672	2410
		0.956	0.833	1900
		1.888	1.121	1540
		3.829	1.629	1060
	88.4	0.659	0.524	2600
		0.939	0.617	1680
		1.878	0.891	1360
		3.755	1.247	950
S-H8	48.4	0.485	0.682	—
		0.969	0.982	—
		2.423	1.530	—
		6.784	2.626	—
	83.4	0.653	0.509	—
		0.942	0.603	—
		1.883	0.903	—
		3.766	1.214	—

[a] β is the slope of the plot $\ln([M_0]/[M])$ vs $1 - \exp(-k_d t/2)$.

lines with slopes close to 0.5, corresponding to the formal propagation reaction order with respect to the initiator concentration (Fig. 2). Therefore, the chain termination by primary radicals (Eq. 9) could be neglected, since β values would not be proportional to the square root of the initiator concentration if chain termination by primary radicals had taken place.

The slopes of the plots of β vs $[I_0]^{1/2}$, shown in Fig. 3, give the ratio $2^{3/2}k_p/k_t^{1/2}(f/k_d)^{1/2}$. Values of $(f/k_d)^{1/2}$ obtained at 30 and 50°C from the data of Talat-Erben and Bywater [10] with $f = 0.45$ [11] and between 70 and 90°C from the data of Redington [12] with $f = 1$, led to the calculated ratio $k_p/k_t^{1/2}$ at these 6 temperatures (Table 2).

The polymerization of styrene-H8 was carried out under the same conditions as the polymerization of styrene-D8 at 48.4 and 83.4°C in order to verify the agreement of our results with the scattered results in the literature (Table 3).

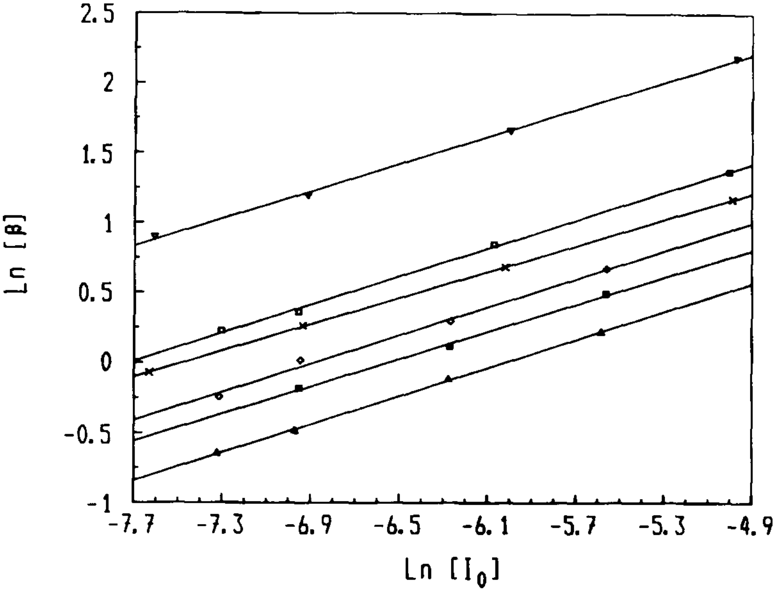


FIG. 2. Log-log plot for β and the initiator concentration $[I_0]$ for the bulk polymerization of styrene-D8 initiated by AIBN at (▽) 28.4 and (×) 48.4°C and by benzoyl peroxide at (□) 68.4, (◇) 78.4, (■) 83.4, and (△) 88.4 ± 0.1°C.

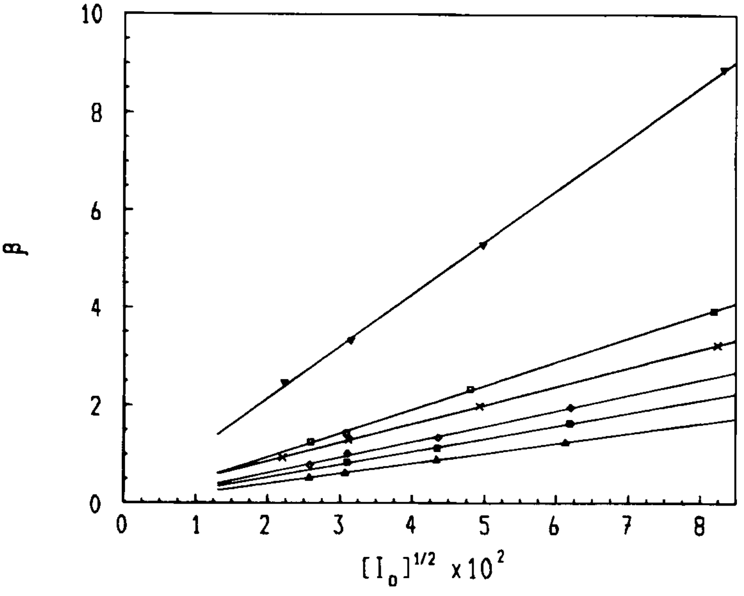


FIG. 3. Variation of β for styrene-D8 as a function of the square root of the initiator concentration at (▽) 28.4, (×) 48.4, (□) 68.4, (◇) 78.4, (■) 83.4, and (△) 88.4 ± 0.1°C.

The activation energy $E_p - E_t/2$ and the frequency factor $A_p - A_t/2$ were determined from the slope and the intercept of the Arrhenius plot of $k_p/k_t^{1/2}$ (Fig. 4). The equation obtained is

$$k_p/k_t^{1/2} = 230 \exp(-24\,000/8.314T). \tag{17}$$

The general equation for the number-average degree of polymerization is given by

TABLE 2. The Ratio $k_p/k_t^{1/2}$ for Styrene-D8 and Styrene-H8 Obtained from the Slopes of β vs $[I_0]^{1/2}$ Plots under the Same Experimental Conditions

	Styrene-D8						Styrene-H8	
Temperature, °C	28.4	48.4	68.4	78.4	83.4	88.4	48.4	83.4
$k_p/k_t^{1/2} \times 10^2$	1.58	2.84	4.83	6.19	7.08	7.56	2.40	5.39

TABLE 3. Comparison between Our Results and the Literature Values of the Ratio $k_p/k_t^{1/2}$ for Styrene-H8

		From			
		Present work	Ref. 11	Ref. 19	Ref. 20
$k_p/k_t^{1/2} \times 10^2$:	48.4°C	2.40	1.75	1.93	1.45
	83.4°C	5.39	5.05	4.61	3.99

$$\bar{P}_n = \frac{\int_0^t -\frac{dM}{dt}\,dt}{\int_0^t [(1/k)R_i + R_M^{tr} + R_S^{tr} + R_I^{tr}]dt}, \tag{18}$$

where the various R^{tr} are the transfer rates, $\bar{P}_n$ is the number-average degree of polymerization, and k is a termination factor depending on the relative importance of the two termination processes described in Rela-

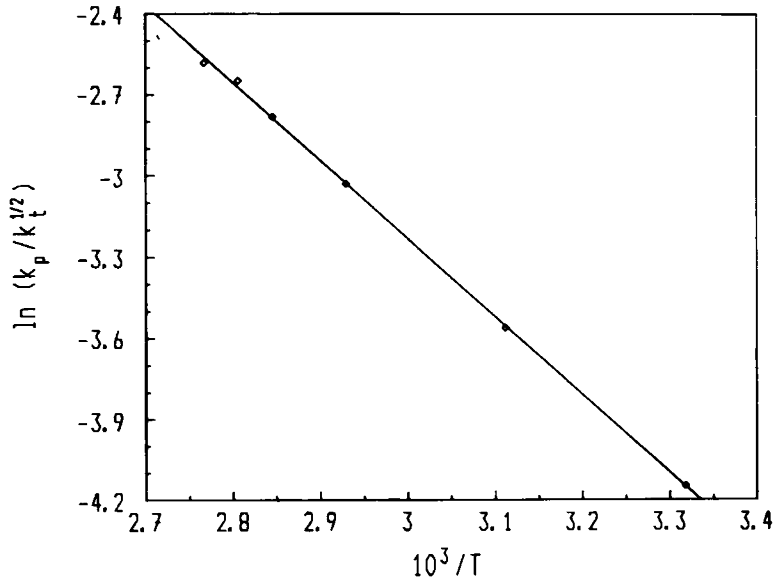


FIG. 4. Arrhenius plot of the ratio $k_p/k_t^{1/2}$ for styrene-D8.

tions (6) and (7): $k = 1$ corresponds to 100% disproportionation (Eq. 6), $k = 2$ correspond to 100% recombination (Eq. 7). The factor k is related to the ratio $\delta = k_t^d/k_t^c$ by the following relation:

$$k = \frac{2(1 + \delta)}{1 + 2\delta}.$$

The experiments were run so as to minimize the effects of transfer to solvent and initiator, allowing the use of Eq. (19) as an approximation.

$$\bar{P}_n^{-1} = \left(\frac{1}{k}\right) \frac{\int_0^t R_i \, dt}{\int_0^t - \frac{dM}{dt} \, dt} + C_M. \tag{19}$$

The assumptions are: 1) bulk polymerization, 2) use of low initiator concentration minimizing transfer to the initiator.

Integration of Eq. (19), with the approximation ln $([M_0]/[M]) = (1 - [M])/[M_0])$ for low conversion, gives

$$\bar{P}_n^{-1} = \left(\frac{k_t^{1/2}}{k_p}\right) \frac{(2fk_d)^{1/2}[I_0]^{1/2}}{[M_0]} \left(\frac{1}{k}\right)\left[\frac{(1 - e^{-k_d t})}{2(1 - \beta)(1 - e^{-k_d t/2}) + \beta(1 - e^{-k_d t})}\right] + C_M. \tag{20}$$

TABLE 4. Values of k_{D8} and k_{H8} Calculated by Eq. (20) from the Degree of Polymerization of Polystyrene-D8 and -HB Initiated by Benzoyl Peroxide and AIBN

	Temperature, °C					
	48.4	68.4	78.4	80.0	83.4	88.4
k_{D8}	1.72	1.59	1.40	1.39[a]	1.49	1.40
k_{H8}	1.67[b]	1.51[c]	1.43[d]	—	—	—

[a] From Ref. 13.
[b] From Ref. 11 at 51.7°C
[c] From Ref. 11 at 69.9°C
[d] From Ref. 11 at 79.9°C.

The values of k were calculated at five temperatures: 50 to 90°C from Eq. (20) and from the data of Table 1.

The results (Table 4) are higher than those calculated from the data of Berger [11] for styrene-H8, which confirms the effect already observed by Hatada et al. [13] at 60°C.

This corroborates the observed deuterium isotopic effect on the mode of termination of methyl methacrylate-D5 [5, 6]. Termination by recombination is predominant in the deuterated compounds. A detailed discussion on this follows.

Nonsteady-State Polymerization

The average lifetimes of the growing polydeuterated styrene-D8 radicals τ_s were determined at 15, 20, and 25°C by the rotating sector method. These polymerizations were followed by dilatometry. This technique requires knowledge of the densities of the monomer and of the monomer-polymer mixture at the concentrations and the temperatures studied. With this end in view, the densities of styrene-D8 were measured at 20, 25, 35, and 40°C (Table 5 and Fig. 5). The linear regression of the data gives the following equation:

$$d_{\mathrm{sty-D8}} = 1.26 - 9.62 \times 10^{-4}\, T, \tag{21}$$

where T is expressed in Kelvins.

Similarly, densities of styrene-D8-polystyrene-D8 mixtures were measured at 25 and 35°C as a function of the percentage of the monomer in the mixture (Table 6). Plots of the data in Fig. 6 give straight lines with the slope

$$\delta d/\delta x = 1.71 \pm 0.0002,$$

where d = density and x = conversion in wt%.

The polymerization rate $(R_p)_s$ under steady-state conditions was measured dilatometrically under constant illumination. By interposing a rotating sector between the polymerization cell and the light source, the

TABLE 5. Density of Styrene-D8

	Temperature, °C			
	20	25	35	40
Density of S-D8	0.9782	0.9733	0.9638	0.9589

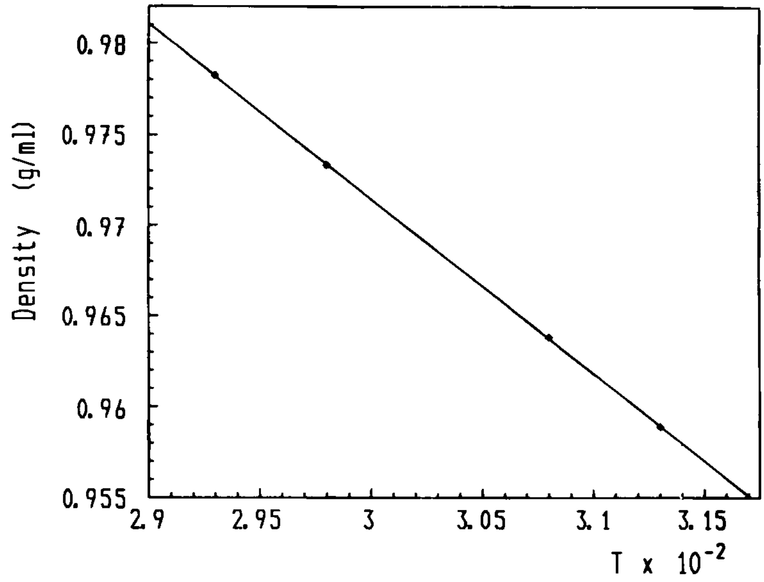


FIG. 5. Variation of the density of styrene-D8 with temperature.

average rate $\bar{R}_p$ was measured at increasing rates of sector rotation. The cycle time as well as t (the length of the light period) and t' (length of the dark period) are determined by the rate of sector rotation. The data are plotted as the rate ratio $\bar{R}_p/(R_p)_s$ vs ln t according to the following equation [7]:

$$\frac{\bar{R}_p}{(R_p)_s} = \frac{(\overline{\mathrm{M}}^\cdot)}{(\mathrm{M}^\cdot)_s} = \frac{1}{(p+1)b}\Bigg\{b + cpb + \ln\left[\frac{1 + (\mathrm{M}^\cdot)_2/(\mathrm{M}^\cdot)_s}{1 + (\mathrm{M}^\cdot)_2/(\mathrm{M}^\cdot)_s c}\right]\left[\frac{1 + (\mathrm{M}^\cdot)_1/(\mathrm{M}^\cdot)_s c}{1 + (\mathrm{M}^\cdot)_1/(\mathrm{M}^\cdot)_s}\right]\Bigg\}, \qquad (22)$$

TABLE 6. Densities of Solutions of PS-D8 in Styrene-D8

	Conversion, %							
Temperature, °C	0	1.03	1.24	2.00	2.08	3.08	4.10	5.15
25	0.9732	0.9784	0.9752	0.9765	0.9767	0.9782	0.9801	0.9818
35	0.9638	0.9656	0.9659	0.9673	0.9674	0.9691	0.9709	0.9727

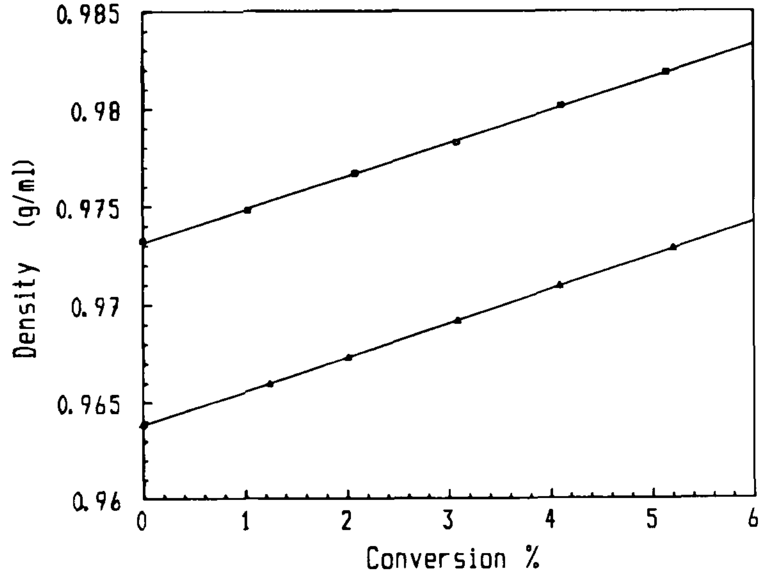


FIG. 6. Variation of the density of polymer solution (PS-D8 in S-D8) as a function of the extent of polymerization (wt%) at (□) 25 and (△) 35°C.

where $(\overline{M^\cdot})$ = the time-average concentration of $M^\cdot$ in intermittent light
$(M^\cdot)_s$ = the concentration of $M^\cdot$ in steady light
$b = t/\tau_s$
$p = t'/t$ (= 3 in our work)
c = steady dark rate/steady light rate
$(M^\cdot)_1$ = concentration of $M^\cdot$ at the beginning of each dark period
$(M^\cdot)_2$ = concentration of $M^\cdot$ at the end of each dark period

Further:

$$\frac{(M^\cdot)_1}{(M^\cdot)_s} = \frac{\tanh b + (M^\cdot)_2/(M^\cdot)_s}{1 + (M^\cdot)_2/(M^\cdot)_s \tanh b}$$

$$\frac{(M^{\cdot})_2}{(M^{\cdot})_s} =$$

$$\frac{(1 - c^2)^2 \tanh^2 b \tanh^2 (cpb) + 4(c \tanh b + \tanh (cpb))(c \tanh b + c^2 \tanh (cpb))]^{1/2}}{2[c \tanh b + \tanh (cpb)]}$$

$$+ \frac{(c^2 - 1) \tanh b \tanh (cpb)}{2[c \tanh b + \tanh (cpb)]}.$$

The experimental curve for the same ratio $p = t'/t$ is adjusted to the theoretical curve $(\bar{R}_p/(R_p)_s$ vs ln (t/τ_s) by using a computer regression program. The best fit between the theoretical and experimental curves yields ln τ_s. Figure 7 shows the theoretical curve fitted with the experimental

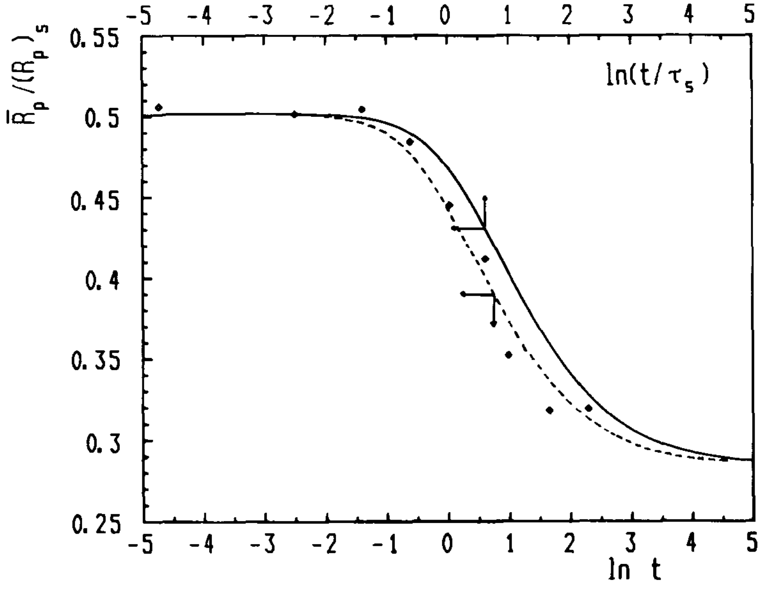


FIG. 7. Determination of the radical lifetime for styrene-D8 at 15°C; (◇) experimental points, (- -) experimental plot, (——) theoretical curve for ratio c = steady rate/steady light rate = 0.045; τ_s = 0.602 s; $\bar{R}_p$, rate of polymerization under intermittent light; $(R_p)_s$, rate of polymerization during steady light.

TABLE 7. Rates of Polymerization (R_p), Average Lifetime of the Growing Polydeuterated Styrene-D8 Radicals (τ_s), and Ratio k_p/k_t Values for the Bulk Polymerization Styrene-D8

Temperature, °C	$R_p \times 10^5$ mol · L^{-1} · s^{-1}	τ,s	$k_p/k_t \times 10^7$
15	1.820	0.602	12.42
20	1.835	0.654	13.75
25	2.650	0.516	15.74

points at 15°C. A knowledge of τ_s permits calculation of the ratio k_p/k_t from the equation

$$\tau_s = \frac{k_p[M]}{k_t(R_p)_s}. \tag{23}$$

The ratio k_p/k_t was determined at 15, 20, and 25°C (Table 7). The Arrhenius plot of ln k_p/k_t vs $1/T$ (Fig. 8) gives

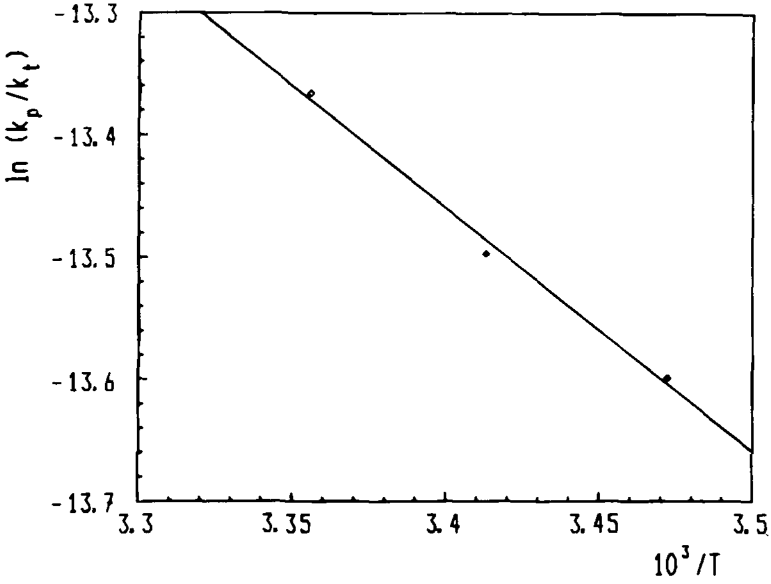


FIG. 8. Arrhenius plot for the ratio (k_p/k_t) for styrene-D8.

$$k_p/k_t = 1.43 \times 10^{-3} \exp(16\,900/8.314T). \tag{24}$$

Combining Eqs. (15) and (21) gives

$$k_p = 3.63 \times 10^{7} \exp(31\,500/8.314T). \tag{25}$$

and

$$k_t = 2.55 \times 10^{10} \exp(14\,200/8.314T). \tag{26}$$

The activation energy for propagation for styrene-D8 is slightly less than that for styrene-H8 (Table 8), while the activation energy of the termination for styrene-D8 is 1.5 times as high as for styrene-H8.

Deuterium Isotope Effect on the Kinetics of Polymerization of Styrene-D8

There are relatively few reports on effects of deuterium substitution on the rate of free-radical polymerizations [1-4, 14]. In the rare example of such studies, the rate of propagation R_p of the isotopically substituted monomers has been found to be greater than that of the normal monomer. This is the case for different substituted styrenes described in Table 9. A secondary inverse isotope effect on the propagation step was observed for all the deuterated monomers, except for the styrenes [4-^{2}H] and [2,4,6-^{2}H$_3$], where no such effects have been reported [2]. The data in Table 9 show that the isotopic effect is independent of temperature in the range from 50 to 85°C. A secondary inverse isotope effect is usually observed when free radicals add to deuterated olefin [15-17]. Pryor [3] compared the rates of

TABLE 8. Activation Energies for Propagation, E_p, and for Termination, E_t, for Styrene-D8 and for Styrene-H8

	$E_p - E_t/2$, kJ/mol	E_p, kJ/mol	E_t, kJ/mol
S-D8	24.02	31.05	14.20
S-H8[a]	28.88	33.57	9.36

[a] FromRef. 11.

TABLE 9. Ratio $[k_p/k_t^{1/2}]_H/[k_p/k_t^{1/2}]_D$ Values for Various Deuterated Styrenes

	Temperature, °C				
	50	60	70	80	85
[α-^{2}H]	0.90[a]	0.91[b]	0.86[d]	—	—
[β-$^2H_2$]	0.86[a]	0.87[b]	0.81[d]	1.0[e]	—
[2,6$^2H_2$]	—	—	0.96[d]	—	—
[2,4,6,-$^2H_3$]	1.0[a]	—	—	—	—
[4-^{2}H]	1.0[a]	—	—	—	—
[2,3,4,5,6-$^2H_5$]	—	0.82[b]	—	—	—
[α,β,2,3,4,5,6−$^2H_8$]	0.84	0.78[c]	—	—	0.78

[a] From Ref. 2.
[b] From Ref. 3.
[c] From Ref. 13.
[d] From Ref. 1.
[e] From Ref. 4.

polymerization of ordinary styrene $(R_p)_H$ and deuterated styrene $(R_p)_D$ at identical styrene and initiator concentrations in the following equation:

$$\frac{(R_p)_H}{(R_p)_D} = \frac{\Delta_H}{\Delta_D} = \frac{(k_p/k_t^{1/2})_H}{(k_p/k_t^{1/2})_D}. \qquad (27)$$

His ratio Δ_H/Δ_D is the same as the ratio reported in Table 9.

Using the model proposed by Pryor [3] pertinent to the prediction of the inverse isotopic effect for the propagation step for styrene-D8, by attributing to each deuterium atom a percentage contribution when free radicals add to carbon-carbon double bonds, a value of 0.66 is obtained for the ratio:

$$\frac{\Delta_H}{\Delta_D} \simeq \frac{(k_p)_H}{(k_p)_D} = 0.66.$$

Values of 0.84 at 48.4°C and 0.78 at 83.4°C are obtained from our results, in good agreement with value of Wittmer [14] (who found $\Delta_H/\Delta_D = 0.78$ at 60°C), rather far from the prediction of the model proposed by Pryor [3]. In this model, the author used the approximation.

$$\frac{\Delta_H}{\Delta_D} = \frac{(k_p)_H}{(k_p)_D}, \qquad (28)$$

neglecting the influence of the isotope effect on the termination step.

Ayrey [5] showed that the latter effect is not to be neglected for methyl methacrylate-D5. He observed an increasing trend in the mode of termination by combination of polymer radicals by passing from MMA-H8 to MMA-D5. He explained the result as an isotope effect on hydrogen transfer during termination by disproportionation. The author concluded that his interpretation could not explain the result of Pryor [2], since polystyrene radicals terminate solely by combination.

Berger [11] also found that the contribution to termination by disproportionation of the polystyrene-H8 radicals is not negligible, which was confirmed recently by Hatada et al. [13] (32% of the termination was found to occur by disproportionation for styrene-H8, and 26% for styrene-D8 at the same temperature). From our results, it seems that such an effect of increasing recombination in the termination step in substituting hydrogen by deuterium appears with styrene. Near 70°C, Berger found a fraction of termination by disproportionation equal to 32% for styrene-H8, while our results give 26% for styrene-D8. A similar effect is observed near 50°C, where disproportionation falls from 22 to 16%. However, our results at 78.4°C (very close to those of other authors [18]) do not confirm such an effect at that temperature. This may be interpreted, as Ayrey [5] did in the case of MMA-D5, as an isotopic effect on deuterium transfer during termination by disproportionation and, consequently, an increase in the mode of termination by recombination.

It is clear that a comparison between the individual constants of termination k_t implies very accurate values, which is not the case even for styrene-H8 (a wide scattering is observed in the literature). This change in the ratio of the two different modes of termination will probably affect the ratio $(k_t)_H/(k_t)_D$ since each mode will induce different isotope effects (disproportionation will give a primary isotope effect, while recombination will give a secondary isotope effect).

CONCLUSIONS

To summarize, steady-state kinetics of radical polymerization of styrene-D8 were carried out at temperature between 30 and 90°C. Also, nonsteady-state kinetics of polymerization of S-D8 were done at 15, 20, and 25°C. The expressions for k_p and k_t were derived by combination of the results of the two kinetic approaches.

The overall activation energy $E_p - E_t/2$ was found to be very close to that of styrene-H8. However, it has been observed that deuteration clearly affects the rate of polymerization through the ratio $k_p/k_t^{1/2}$. Particularly, the data show that the deuterium isotope effect affects not only the propagation step of the polymerization of styrene-D8 but also the termination step. An increase in termination by combination results when the hydrogen atoms are substituted by deuterium atoms.

REFERENCES

[1] K. R. Kopecky and S. Evans, *Can. J. Chem., 47,* 4049 (1969).
[2] R. Kirchner, *Makromol. Chem., 96,* 179 (1966).
[3] W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Am. Chem. Soc., 88,* 1199 (1966).
[4] G. S. Hammond and K. R. Kopecky, *J. Polym. Sci., 60,* S54 (1962).
[5] G. Ayrey and D. J. D. Wong, *Polymer, 16,* 623 (1975).
[6] K. Hatada, T. Kitayama, and H. Yuki, *Makromol. Chem., Rapid Commun., 1,* 51 (1980).
[7] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc., 71,* 497 (1949).
[8] K. C. Berger, P. C. Deb, and G. Meyerhoff, *Macromolecules, 10,* 5 (1977).
[9] G. Goldfinger and K. E. Lauterbach, *J. Polym. Sci., 3,* 2 (1948).
[10] M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc., 77,* 3712 (1955).
[11] K. C. Berger, *Makromol. Chem., 176,* 3575 (1975).
[12] L. E. Redington, *J. Polym. Sci., 3,* 4 (1948).
[13] K. Hatada, T. Kitayama, and E. Masuda, *Polym. J., 17,* 985 (1985).
[14] P. Wittmer, H. Bock, H. Naarmann, and B. J. Schmitt, *Makromol. Chem., 182,* 2505 (1981).
[15] D. B. Denny and N. Tunkel, *Chem. Ind. (London),* p. 1383 (1959).
[16] M. Feld, A. P. Stefant, and M. Szwarc, *J. Am. Chem. Soc., 84,* 4451 (1962).
[17] M. Matsulka and M. Szwarc, *Ibid, 83,* 1260 (1961).
[18] K. Hatada, T. Kitayama, and E. Masuda, *Polym. Prepr., Jpn., 34,* 1296 (1985).
[19] G. Henrici-Olive and S. Olive, *Adv. Polym. Sci., 2,* 496 (1961).
[20] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc., 73,* 1700 (1951).

Received November 30, 1988
Revision received February 26, 1989